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TRANSFORMATION REACTION AND CORROSION BEHAVIOUR OF TWO ZIRCONIUM-COPPER-MOLYBDENUM ALLOYS

H. M. SKELLY AND C. F. DIXON

PHYSICAL METALLURGY DIVISION

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TRANSFORMATION REACTION AND CORROSION BEHAVIOUR OF TWO ZIRCONIUM-COPPER-MOLYBDENUM ALLOYS

by

H.M. Skelly* and C.F. Dixon**

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ABSTRACT

The transformation reaction for a Zr-1.0%Cu-1.5%Mo alloy quenched from the beta phase (1000°C, 1830°F) and aged at 500°C (930°F) was shown to be:

$$\text{omega}+\text{beta} \rightarrow \text{alpha prime} \rightarrow \text{alpha}+Zr_2Cu+ZrMo_2$$

The corrosion resistance of this alloy and of a Zr-0.5%Cu-0.5%Mo alloy was found to be related to the structures produced by the transformation reaction - optimum corrosion resistance was obtained after aging for 32 and 24 hr, respectively.

Aging of specimens resulted in an increase in the size of the intermetallic particles; and larger $ZrMo_2$ particles in overaged specimens appeared to corrode at a rate greater than the matrix, causing cracking of the corrosion film and resulting in an accelerated corrosion rate for the specimens.

The type of corrosion film, like the corrosion rate, was affected by structural changes produced by the transformation reaction.

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Direction des mines

Rapport de recherches R 204

RÉACTION DE TRANSFORMATION ET RÉSISTANCE A LA CORROSION DE DEUX ALLIAGES DE ZIRCONIUM-CUIVRE-MOLYBDÉNE

par H. M. Skelly* et C. F. Dixon**

RÉSUMÉ

L'alliage Zr-1.0%Cu-1.5%Mo trempé à partir de la phase bêta (1000°C, 1830°F) et vieilli à 500°C (930°F) a manifesté les réactions de transformation suivantes:

oméga+bêta → alpha prime → alpha+Zr_2Cu+$ZrMo_2$

La résistance à la corrosion de cet alliage et de delui de formule Zr-0.5%Cu-0.5%Mo est en rapport avec les structures produites par les réactions de transformation. La résistance maximale s'est manifestée après vieillissement de 32 et 24 heures respectivement.

Le vieillissement des échantillons a entraîné un accroissement de la taille des particules intermétalliques, tandis que les plus grosses particules de $ZrMo_2$ des échantillons survieillis se sont corrodées d'une manière plus importante que la matrice, provoquant la fissuration du film de corrosion et accélérant la vitesse de corrosion des échantillons.

Le type de film de corrosion et la vitesse de corrosion ont subi des variations dues aux changements structuraux provoqués par les réactions de transformation.

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INTRODUCTION

The object of this investigation was to determine the transformation reaction of a Zr-1.0%Cu-1.5%Mo alloy quenched from the beta phase and aged at 500°C (930°F), and also to observe any anomalies in its corrosion behaviour during transformation when tested in steam at 400°C (750°F) and 1500 psi. The corrosion behaviour of a second alloy, Zr-0.5%Cu-0.5%Mo, that was shown in previous work[1] to have transformation reactions similar to the above alloy, was also examined. In addition, microexaminations were made of the corrosion film during transformation and an electron-probe microanalyser was used to investigate the composition of the intermetallic phases.

EXPERIMENTAL PROCEDURE

Alloy Preparation

The materials used to prepare the experimental alloys are listed in Table 1, and melt identifications with nominal compositions of the alloys are given in Table 2.

All the alloy melts except FJ(Zr-1%Cu-1.5%Mo) were prepared in a laboratory-size tungsten-arc furnace. Melting and alloying were carried out by striking an arc between a tungsten electrode and the charge contained in a water-cooled copper hearth. Melting was carried out in an argon atmosphere at a pressure of 350 mm mercury, and each alloy was remelted at least four times to ensure homogeneity. The resultant ingot was cigar-shaped and weighed approximately 75 grams.

Melt FJ was prepared in a consumable-electrode arc-melting furnace. First, a master alloy consisting of 1 part zirconium + 1 part copper + 1.5 parts molybdenum was prepared in a tungsten-arc furnace. The master alloy was then pressed with zirconium sponge to form an electrode, which was melted under vacuum in a consumable-electrode furnace to give a 3-in.-diameter ingot weighing 1½ lb. This ingot was cut into pieces

weighing approximately 75 g, which were melted into cigar-shaped ingots in a tungsten-arc furnace.

All the cigar-shaped ingots, except melt KU, were hot-swaged in air at 700°C (1290°F) into 0.35-in.-diameter rods. These rods, with the exception of the one swaged from melt FM (Zr-0.5%Cu-0.5%Mo), were hot-rolled at 700°C (1290°F) to sheet 0.20 in. thick.

Melt KU, with a high alloy content (Zr-3.0%Cu-4.5%Mo), was prepared to facilitate identification of intermetallic phases.

In addition to the above laboratory-prepared material, a Zr-1.0%Cu-1.5%Mo alloy sheet 0.062 in. thick was obtained from Imperial Chemical Industries Limited (I.C.I.), Birmingham, England.

Transformation Reactions

Specimens 1 in. x 5/16 in. x 5/64 in., to be used for transformation reaction studies, were machined from the hot-rolled Zr-1.0%Cu-1.5%Mo alloy (melts FL and FJ). These specimens were heat-treated in vacuum for 1 hr at temperatures ranging from 800°C (1470°F) to 1000°C (1830°F), and then water-quenched. The specimens quenched from 1000°C (1830°F) were aged at 500°C (930°F) for 2, 8, 30 min, and 1, 4, 48 and 100 hr. Microexamination and X-ray diffraction analysis were carried out on all specimens.

Intermetallic Phases

Specimens (1 in. x 5/16 in.) of the I.C.I. sheet material were examined by an electron-probe microanalyser to determine the composition of the intermetallic phases. Some specimens were solution heat-treated in vacuum for 1 hr at 1000°C (1830°F), water-quenched, then aged at 500°C (930°F) for 100 hr; in an attempt to coalesce the intermetallics, other specimens were heat-treated in vacuum at 1000°C (1830°F) for 1 hr, then cooled at 5.5°C/hr (10°F/hr) to 550°C (1020°F), and water-quenched. An arc-melted specimen of the Zr-3.0%Cu-4.5%Mo alloy (melt KU) was also examined by the electron microscope.

Corrosion Testing

Specimens, 1 in. x 5/16 in. x 5/64 in., for corrosion testing were machined from hot-rolled Zr-1.0%Cu-1.5%Mo and Zr-0.5%Cu-0.5%Mo alloys (melts FL and FN respectively). These specimens, with 1-in. x 5/16-in. specimens of the I.C.I. sheet material, were heat-treated in vacuum at 1000°C (1830°F) for 1 hr, and water-quenched. This was followed by aging at 500°C (930°F) for times up to 100 hr.

Corrosion tests were carried out in an autoclave in steam at 400°C (750°F) and 1500 psi. The specimens were removed periodically for weighing, and the water was changed after each weighing.

Microexamination of Corrosion Films

For corrosion film studies, specimens 1 in. in length were cut from Zr-0.5%Cu-0.5%Mo swaged bar (melt FM). The specimens were corrosion-tested in the following heat-treated conditions:

(a) heated in vacuum for 1 hr at 1000°C (1830°F), and water-quenched;

(b) heated in vacuum for 1 hr at 1000°C (1830°F), water-quenched, and then aged at 500°C (930°F) for 8, 24 and 100 hr;

(c) annealed at 700°C (1290°F) for 1 hr.

One end of each specimen was ground flat and chemically polished for electron microexamination prior to corrosion testing. The specimens were then corrosion-tested in steam for 24 hr and the resulting corrosion films formed on the polished ends were examined by the electron microscope.

Metallography

For metallographic examination, X-ray diffraction analysis, electron photomicrography, and electron probe micro-analysis, the specimens were polished on silicon-carbide abrasive paper to a 600 grit, and then on microcloth with Linde A compound as the abrasive. This was followed by chemical polishing

in a solution containing 45 cc nitric acid, 45 cc distilled water, and 8-10 cc hydrofluoric acid.

To etch for the Zr-Mo intermetallic, which was also visible after chemical polishing, specimens were immersed for 30 sec in a solution containing 20 cc hydrofluoric acid, 20 cc nitric acid and 60 cc glycerin. To reveal only the Zr-Cu intermetallic, polished specimens were immersed for 30 sec in a solution containing 1 cc hydrofluoric acid, 1 cc nitric acid and 98 cc distilled water.

EXPERIMENTAL RESULTS

Transformation Reactions

Results of X-ray diffraction analysis of specimens of the Zr-1.0%Cu-1.5%Mo alloy when quenched from 800°C (1470°F) showed the structure to consist of alpha, omega (a transformation phase) and beta phases. Metallographic examination of these specimens showed the alpha phase as pools of equilibrium alpha that had been retained from the quenching temperature. This structure is illustrated in the photomicrograph in Figure 1.

Specimens heat-treated at 850°C (1560°F) and 900°C (1650°F) had similar structures to those heat-treated at 800°C (1470°F), except that the amount of alpha phase present decreased as the heat-treating temperature increased (see Figures 1 to 3). When specimens were heat-treated at 1000°C (1830°F) there was no visible alpha in the as-quenched structure (Figure 4), and X-ray diffraction analysis showed this quenched structure to consist mainly of the omega phase with some beta phase.

The changes in structure of specimens water-quenched from 1000°C (1830°F) and aged at 500°C (930°F) for times up to 100 hr were followed by means of X-ray diffraction analysis and metallographic examination. The results of the X-ray diffraction analysis, listed in Table 3, show that the omega and beta phases present after quenching transformed

to alpha prime after aging for 8 min. After aging for 30 min, precipitation of intermetallics was evident; and after 4 hr the alpha prime had transformed to equilibrium alpha.

The alpha prime phase is illustrated in the photomicrograph of a specimen aged for 30 min, shown in Figure 5. A progressive precipitation of the intermetallics with aging time can be seen by comparing the photomicrographs in Figures 6, 7 and 8, showing specimens of the Zr-1.0%Cu-1.5%Mo alloy aged for 4, 48 and 100 hr respectively.

Intermetallic Phases

Intermetallic phases present in Zr-1.0%Cu-1.5%Mo alloy specimens heat-treated at 1000°C (1830°F) for 1 hr and aged at 500°C (930°F) for 100 hr, were not large enough for qualitative analysis when examined with the electron-probe microanalyser. However, a Zr-Mo phase and a Zr-Cu phase were detected, and preferential etching revealed these phases as shown in the photomicrographs in Figures 9 and 10 respectively.

Electron-probe microanalysis of specimens that had been heat-treated at 1000°C (1830°F) for 1 hr, cooled at 5.5°C/hr (10°F/hr) to 550°C (1020°F), and then water-quenched, showed one intermetallic phase to be Zr_2Cu, but the Zr-Mo phase could not be identified. This heat treatment, which was intended to coalesce the intermetallics, caused the Zr_2Cu phase to precipitate as particles and the Zr-Mo phase to be distributed along alpha platelet boundaries. A photomicrograph of this specimen is shown in Figure 11.

Electron-probe microanalysis of an arc-melted specimen of the Zr-3%Cu-4.5%Mo alloy identified a $ZrMo_2$ phase. The $ZrMo_2$ in this specimen was present as particles (Figure 12) surrounded by the Zr_2Cu (Figure 13). Figures 14, 15 and 16 are electron-probe X-ray-scan photographs of this alloy which illustrate the distribution of the molybdenum-, copper- and zirconium-rich phases.

Corrosion Testing

The results of the corrosion tests on specimens of the Zr-1.0%Cu-1.5%Mo and Zr-0.5%Cu-0.5%Mo alloys are shown in Figure 17 as plots of weight gain versus time of aging at 500°C (930°F). The corrosion results for the Zr-1.0%Cu-1.5%Mo alloy show that the weight gain varied by a factor of 20, depending on the time of aging. The corrosion rate was at a maximum for specimens aged for 1 hr and 95 hr, and at a minimum for specimens aged for 32 hr.

The corrosion results for the Zr-0.5%Cu-0.5%Mo alloy, also plotted in Figure 17, show that the weight gains for specimens of this alloy again depended on the aging time, with a minimum occurring after aging for 24 hr.

Short corrosion times (300 hr for the Zr-0.5%Cu-0.5%Mo alloy and 400 hr for the Zr-1.0%Cu-1.5%Mo alloy) were used to determine the curves, because the corrosion film on some of the specimens--particularly those aged for longer periods and exhibiting large weight gains--began to spall if the tests were continued for longer times.

Types of Corrosion Films

Corrosion films on specimens of the Zr-1.0%Cu-1.5%Mo alloy after testing for 400 hr were of four distinct types, depending on the aging time. These films are shown in Figure 18, and discussed below:

1. Films on specimens in the as-quenched condition, and on specimens aged up to 8 min, had a mottled appearance with light and dark areas resembling a grain-like structure. This film can be seen on specimen 1 in the photograph, Figure 18. Figure 19 is a photomicrograph of a cross section showing a difference in film thickness on adjacent areas, and Figure 20 shows the same field after anodizing. It is evident that the two grain-like areas have different orientations. X-ray diffraction analysis

showed the omega and beta phases in this structure to have similar orientations within each area.

2. Specimens aged for 30 min to 4 hr had a black film, as shown on specimen 2 in Figure 18. Figure 21 is a photomicrograph of a cross-section of this film.
3. Specimens aged for 24 and 48 hr had a thin black film, with a white adherent film forming, in areas, over the black. This black film is shown on specimen 4 in Figure 18, and a cross section is shown in the photomicrograph in Figure 22.
4. After aging for 72 and 100 hr, corrosion specimens acquired a white film that had a tendency to spall. Specimen 3 in Figure 18 is an example. Figure 23 is a photomicrograph of a cross section of the white film.

Information on these various films is given in Table 4.

Microexamination of Corrosion Films

Electron micrographs of specimens of alloy Zr-0.5%Cu-0.5%Mo, after aging for 0, 8, 24 and 100 hr and after annealing, are shown in Figures 24 to 28, respectively. Figure 24 shows that there were few intermetallic particles in specimens quenched from 1000°C (1830°F). On aging, intermetallic particles began to appear; their size increased with time, and their number also increased initially then decreased (see Figures 25, 26 and 27). The annealed specimen, shown in Figure 28, exhibited the largest intermetallic particles.

After being corrosion-tested for 24 hr, the zirconium oxide film remained adherent on specimens quenched from 1000°C (1830°F) and on specimens aged for 24 hr (see Figures 29 and 30 respectively). However, in the case of the specimens that contained large particles, i.e. those aged for 100 hr (Figure 27) and those annealed (Figure 28), the corrosion film broke up because

of cracking around the enlarged intermetallic particles, as is shown in the photomicrographs in Figures 31 and 32 respectively.

DISCUSSION

Transformation Reactions

Specimens of the Zr-1.0%Cu-1.5%Mo alloy that were quenched from 800°C (1470°F), 850°C (1560°F) and 900°C (1650°F) contained alpha, beta and omega phases. These specimens were evidently quenched from the alpha + beta phase region, and the copper and molybdenum were held in solid solution on quenching.

Specimens quenched from 1000°C (1830°F) contained only the omega and beta phases, indicating that these specimens had been in the beta phase region and that the copper and molybdenum were again held in solid solution on quenching.

It has been shown that on aging the specimens quenched from 1000°C (1830°F), the omega and beta phases transformed to alpha prime which also retained the copper and molybdenum in solid solution (Table 3). On further aging (30 min), the copper and molybdenum began to precipitate as intermetallics and the X-ray diffraction lines of the alpha prime phase gradually transformed to the sharp lines of equilibrium alpha phase.

It is concluded that the transformation reaction of the Zr-1.0%Cu-1.5%Mo alloy, after quenching from 1000°C (1830°F) and aging at 500°C (930°F), is as follows:

omega + beta → alpha prime → alpha + intermetallics

and that, from results in previous work[1], the Zr-0.5%Cu-0.5%Mo alloy can be expected to have a similar transformation reaction.

Intermetallic Phases

To be in agreement with the Phase Rule, the maximum number of intermetallic phases that could be present in the Zr-Cu-Mo alloys examined would be two. Results from electron-probe microanalysis of heat-treated specimens of the Zr-1.0%Cu-1.5%Mo alloy showed the presence of a Zr_2Cu phase and of a Zr-Mo intermetallic phase that could not be identified because of its size or shape. Microexamination of specimens of this alloy showed that the mode of precipitation of the intermetallics varied, depending on the heat treatment.

To obtain the Zr-Mo intermetallic particles in a form suitable for qualitative analysis by the electron probe, the Zr-3.0%Cu-4.5%Mo alloy was prepared. In specimens of this alloy the Zr-Mo phase appeared as particles large enough for identification as $ZrMo_2$ (Figure 12).

Because there is only one intermetallic in the Zr-Mo system, i.e. $ZrMo_2$, and because this phase was identified in the Zr-3.0%Cu-4.5%Mo arc-melted specimen, it was concluded that $ZrMo_2$ would be the Zr-Mo phase present in the Zr-1.0%Cu-1.5%Mo alloy specimens.

Corrosion Testing

The oxide film that forms on zirconium and its alloys during corrosion is known to be an anion-deficit semiconductor[2,3], with corrosion occurring by oxygen diffusing through the film then reacting at the oxide/metal interface. According to the Hauffe theory[4], the addition of alloying elements having a higher valence than zirconium would decrease the number of oxygen ion defects, retard the diffusion of oxygen, and reduce the corrosion rate. Because an important condition for the Hauffe theory to apply is that the alloying elements must be in solid solution with zirconium in order to share in film formation, this theory will not apply when intermetallics are present.

As previously mentioned, when the Zr-1.0%Cu-1.5%Mo alloy was water-quenched from 1000°C (1830°F), the copper and molybdenum were held in solid solution in the omega and beta

phases (Table 3), as shown by the electron micrograph in Figure 24; the copper and molybdenum were also held in solid solution in the Zr-0.5%Cu-0.5%Mo alloy specimens quenched from 1000°C (1830°F). In this situation the Hauffe theory would apply, and it can be concluded, from corrosion rates of the quenched specimens of both these alloys (Figure 17), that the solution of copper and molybdenum was unfavourable for good corrosion resistance.

As aging commenced and the copper and molybdenum began to precipitate as fine intermetallics, the corrosion resistance improved. In this case, the Hauffe theory would not apply; the reason for the improved corrosion resistance at this stage is not known, but it appears to be related to the change in structure from the omega plus beta to alpha and to the presence of fine intermetallics. On further aging, as the $ZrMo_2$ particles increased in size, it was evident that they corroded at a faster rate than the matrix and eventually, because of their size, caused cracking in the corrosion film. This resulted in an increase in the corrosion rate of the specimen.

There was no evidence that Zr_2Cu had any influence on the corrosion behaviour of the alloys.

Types of Corrosion Films

The mottled corrosion film on specimens of the Zr-1.0%Cu-1.5%Mo alloy quenched from 1000°C (1830°F) and aged up to 8 min (see specimen 1 in Figure 18) was concluded to be the result of preferential corrosion on grain-like areas that were the outlines of beta grains that had been present when the specimens were at 1000°C (1830°F). Because the beta and omega phases in each area had similar orientations, it appears that these phases had anisotropic corrosion properties.

As aging progressed, the corrosion resistance increased and the thickness of the film decreased. After aging for 48 hr, the black film was only 5 microns thick (Table 4).

The white film on specimens aged for longer periods (72 and 100 hr) most likely resulted from accelerated corrosion of the $ZrMo_2$ particles, with subsequent cracking of the corrosion film leading to increased corrosion rates.

The type of corrosion film, then, like the corrosion rate, was dependent on the heat treatment. This is emphasized by comparing the dark film on specimens of the Zr-1.0%Cu-1.5%Mo alloy aged for 48 hr (Figure 22) with the white film on specimens aged for 100 hr (Figure 23).

CONCLUSIONS

1. The presence of two intermetallics in the Zr-Cu-Mo alloys was established. One intermetallic was positively identified as Zr_2Cu, and the other intermetallic was tentatively identified as $ZrMo_2$.

2. The zirconium alloy Zr-1.0%Cu-1.5%Mo aged according to the reaction:

omega + beta→alpha prime→equilibrium alpha + $ZrMo_2$+Zr_2Cu

when water-quenched from the beta phase (1000°C, 1830°F) and aged at 500°C (1930°F).

3. The weight gain of specimens of the Zr-1.0%Cu-1.5%Mo alloy during corrosion testing at 400°C (750°F) and 1500 psi varied by a factor of 20, depending on the heat treatment. Minimum weight gains were observed after specimens were aged for 32 hr.

4. The omega and beta phases in the quenched structure of the Zr-1.0%Cu-1.5%Mo alloy specimens had anisotropic corrosion properties.

5. Depending on the heat-treatment given Zr-1.0%Cu-1.5%Mo specimens, four different types of corrosion film were observed.

6. The corrosion rate of the Zr-0.5%Cu-0.5%Mo alloy was also shown to depend on the heat treatment. The minimum corrosion rate for this alloy was obtained on specimens aged for 24 hr.

Over-aging of the Zr-0.5%Cu-0.5%Mo alloy resulted in an increase in the size of the $ZrMo_2$ particles. These particles corroded faster than the matrix and eventually, because of their size, caused cracking in the corrosion film, resulting in an accelerated corrosion rate for the specimens.

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REFERENCES

1. C.F. Dixon, "Transformation Reaction and Mechanical Properties of Zirconium Alloys Containing Copper and Molybdenum". Physical Metallurgy Division, Internal Report PM-R-60-6 (1960).

2. W.M. Mallett and W.M. Albrech, "High Temperature Oxidation of Two Zirconium-Tin Alloys". J. Electrochem. Soc. 102(7), 407-414 (1955).

3. H.A. Porte, J.G. Schnizlein, R.C. Vogel and D.F. Fischer, "Oxidation of Zirconium and Zirconium Alloys". J. Electrochem. Soc. 107(6), 506-515 (1960).

4. O. Kubaschewski and B.E. Hopkins, "Oxidation of Metals and Alloys". Butterworth Scientific Publications, London, 120-130 (1953).

TABLE 1

Material Used

Metals	Purity	Source
Zirconium Sponge	Reactor Grade	Carborundum Metals Co.
Copper	99.99%	American Metals Climax Inc.
Molybdenum	99.5%	Sylvania Electric Products Inc.

TABLE 2

Alloy Compositions

Melt Identification	Nominal Composition		
	Cu, %	Mo, %	Zr, %
FN	0.5	0.5	Remainder
FM	0.5	0.5	"
FL	1.0	1.5	"
FH	1.0	1.5	"
FJ	1.0	1.5	"
KU	3.0	4.5	"
(I.C.I. Material*)	1.0	1.5	"

*Obtained from Imperial Chemical Industries Limited, Birmingham, England.

TABLE 3

Aging Reaction of Zr-1.0%Cu-1.5%Mo Alloy
Quenched from 1000°C (1830°F), Aged at 500°C (930°F)

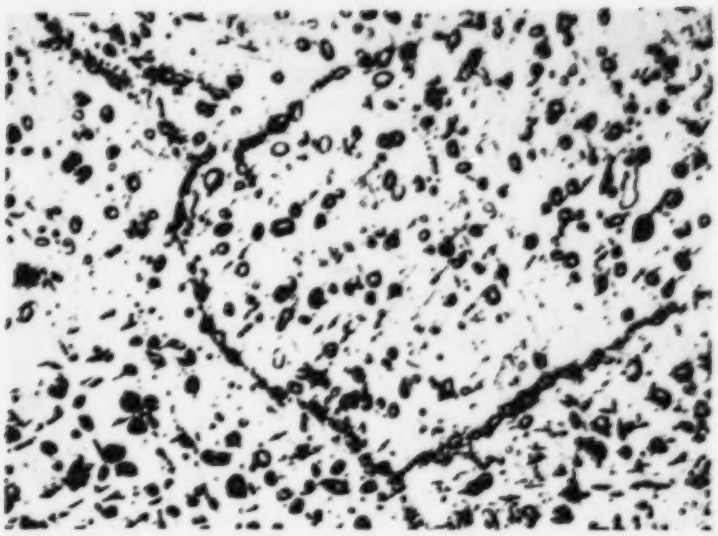
Aging Time	Phases Present
0	Omega + some beta
2 min	Omega + some beta
8 min	Alpha prime
30 min	Alpha prime + intermetallics
1 hr	Alpha prime + intermetallics
4 hr	Alpha + intermetallics
48 hr	Alpha + intermetallics
100 hr	Alpha + intermetallics

TABLE 4

Corrosion Films on Zr-1.0%Cu-1.5%Mo Alloy
After 400 Hours in Steam at 400°C (750°F) and 1500 psi

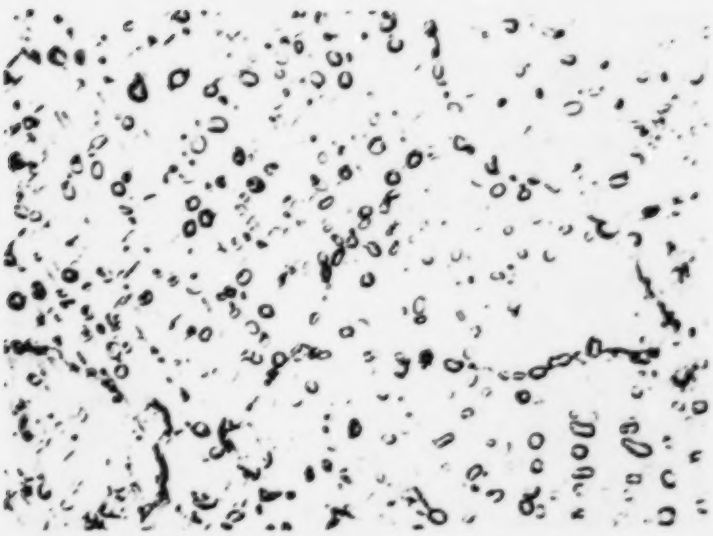
Aging Time	Film Appearance	Film Thickness (microns)	Wt. Gain of Specimen (mg/dm^2)*
0-8 min	Mottled	42 and 56	650 to 800
4 hr	Black	42	400
48 hr	Black & White	5 (Black)	80
100 hr	White	96	1150

* Average of two specimens.



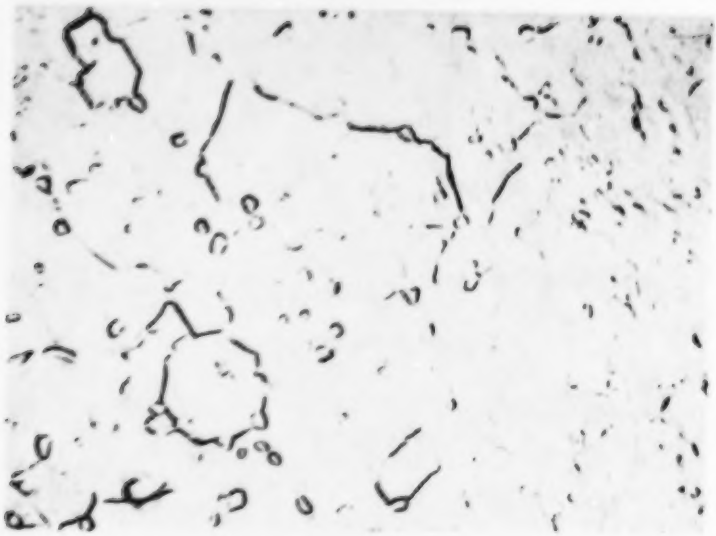
X750

Figure 1: Zr-1.0%Cu-1.5%Mo.
Heat-treated 800°C (1470°F), WQ.
As polished.



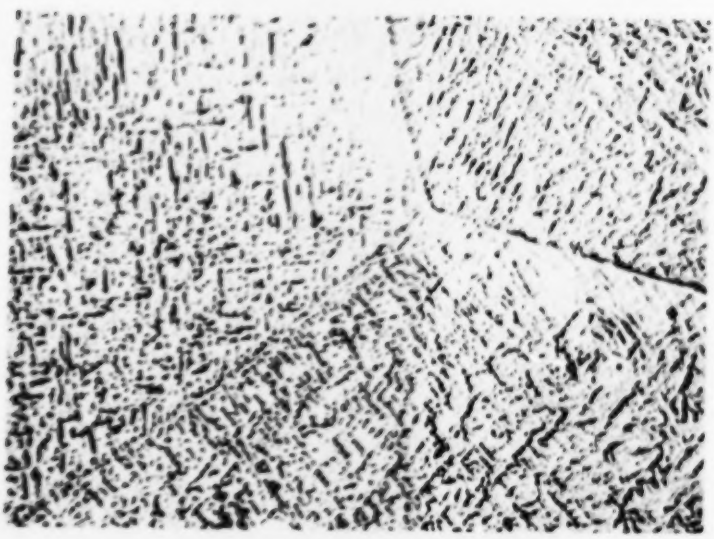
X750

Figure 2: Zr-1.0%-Cu-1.5%Mo.
Heat-treated 850°C (1560°F), WQ.
As polished.



X750

Figure 3: Zr-1.0%Cu-1.5%Mo.
Heat-treated 900°C (1650°F), WQ.
As polished.

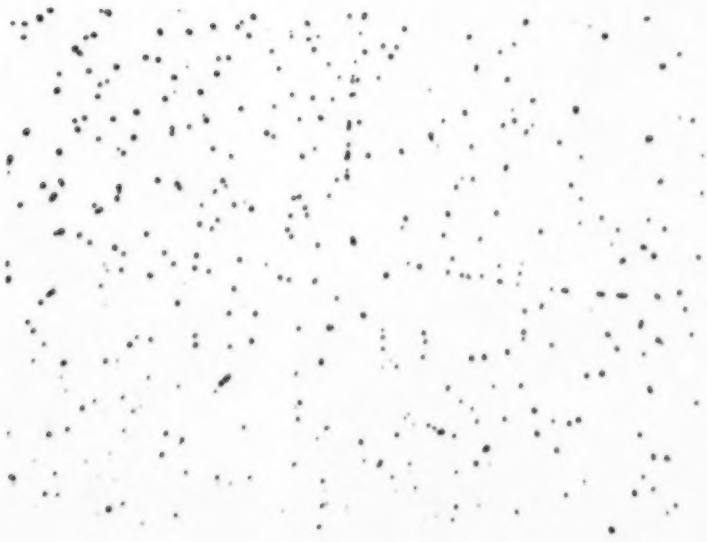


X750

Figure 4: Zr-1.0%Cu-1.5%Mo.
Quenched from 1000°C (1830°F),
aged 500°C (930°F) for 2 min.
As polished.

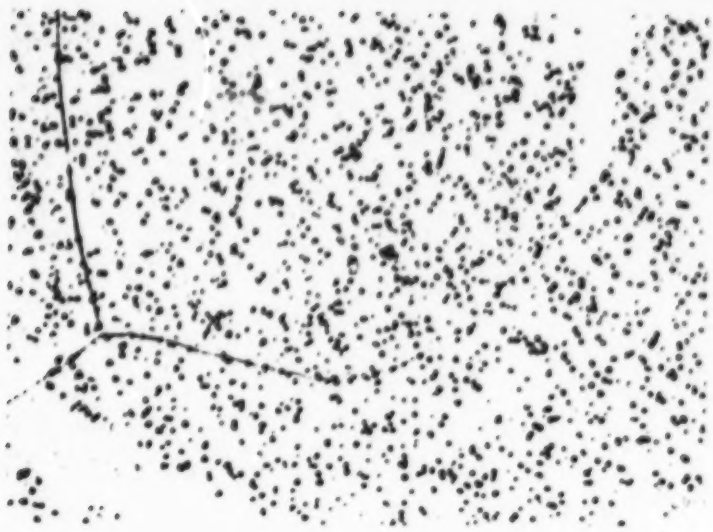
X750

Figure 5: Zr-1.0%Cu-1.5%Mo.
Quenched from 1000°C (1830°F),
aged 500°C (930°F) for 30 min.
As polished.
Oblique illumination.



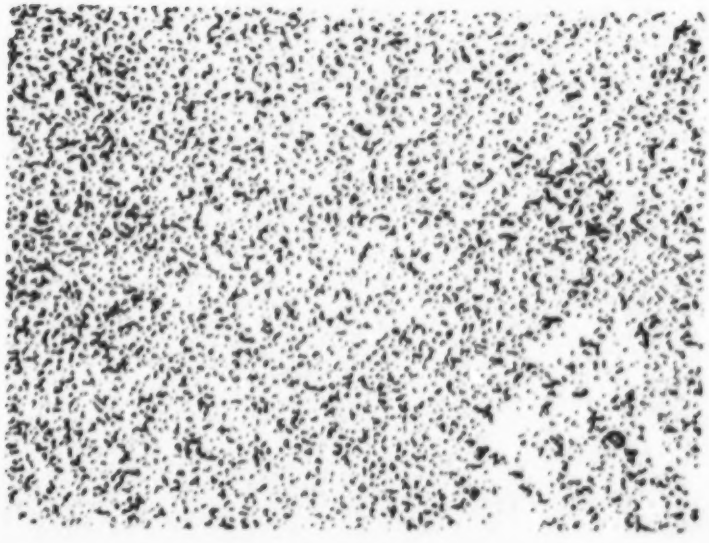
X750

Figure 6: Zr-1.0%Cu-1.5%Mo.
Quenched from 1000°C (1830°F),
aged 500°C (930°F) for 4 hr.
As polished.



X750

Figure 7: Zr-1.0%Cu-1.5%Mo.
Quenched from 1000°C (1830°F),
aged 500°C (930°F) for 48 hr.
As polished.

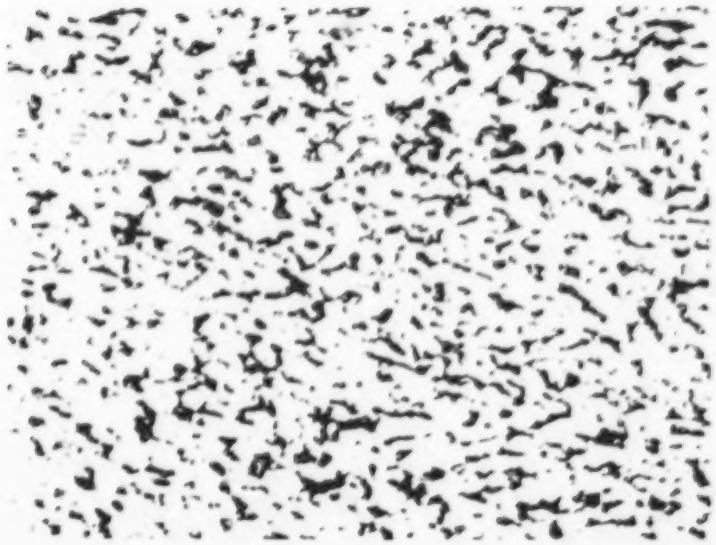


X750

Figure 8: Zr-1.0%Cu-1.5%Mo.
Quenched from 1000°C (1830°F),
aged 500°C (930°F) for 100 hr.
As polished.

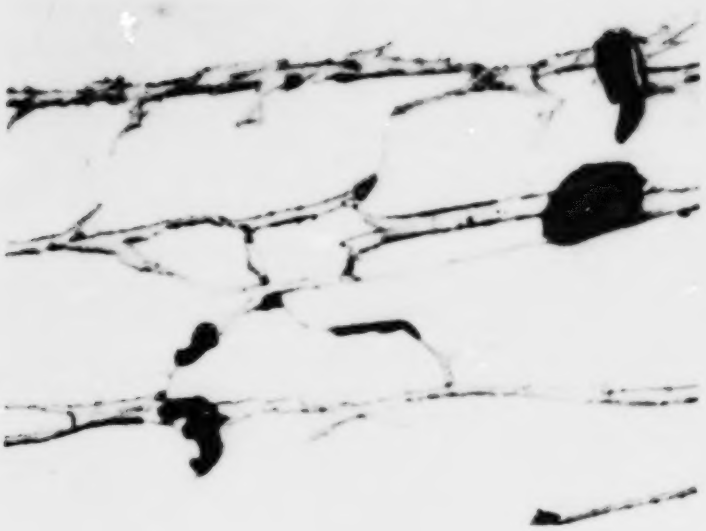
X1000

Figure 9: Zr-1.0%Cu-1.5%Mo alloy (ICI).
Heat-treated 1000°C (1830°F) 1 hr, WQ,
aged 500°C (930°F) 100 hr.
Etched for Zr-Mo phase.



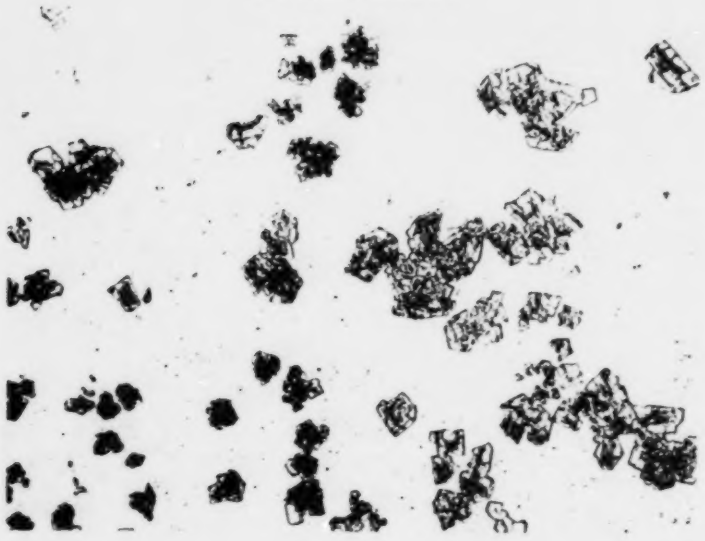
X1000

Figure 10: Zr-1.0%Cu-1.5%Mo alloy (ICI).
Heat-treated 1000°C (1830°F) 1 hr, WQ,
aged 500°C (930°F) 100 hr.
Etched for Zr-Cu phase.



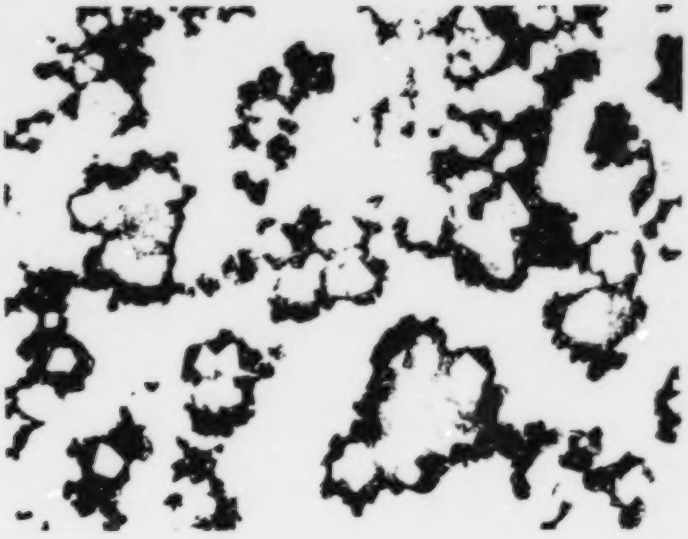
X1000

Figure 11: Zr-1.0%Cu-1.5%Mo alloy (ICI).
Heat-treated 1000°C (1830°F) 1 hr and cooled at 5.5°C/hr (10°F/hr) to 550°C (1020°F), then WQ.
As polished.



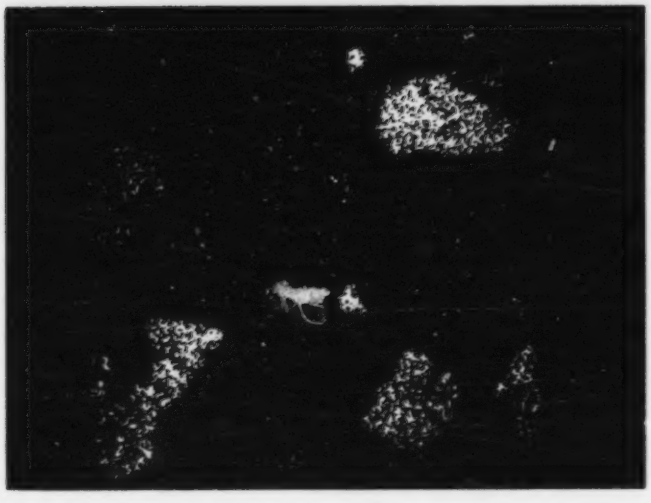
X400

Figure 12: Zr-3.0%Cu-4.5%Mo alloy (Melt KU).
Arc-melted.
Etched for Zr-Mo phase.



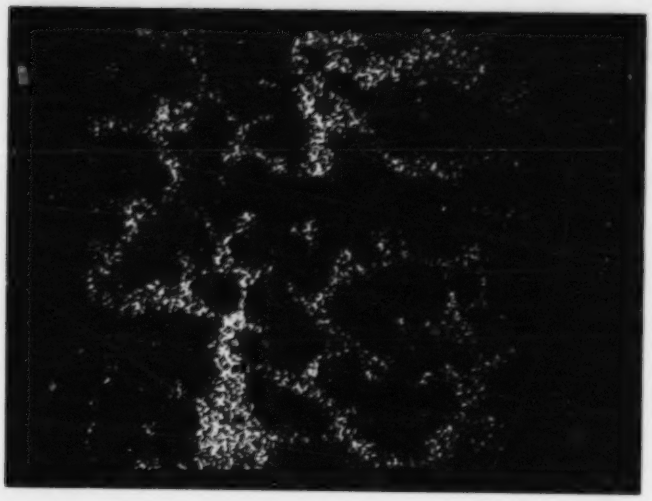
X400

Figure 13: Zr-3.0%Cu-4.5%Mo alloy (Melt KU).
Arc-melted.
Etched for Zr-Cu phase.



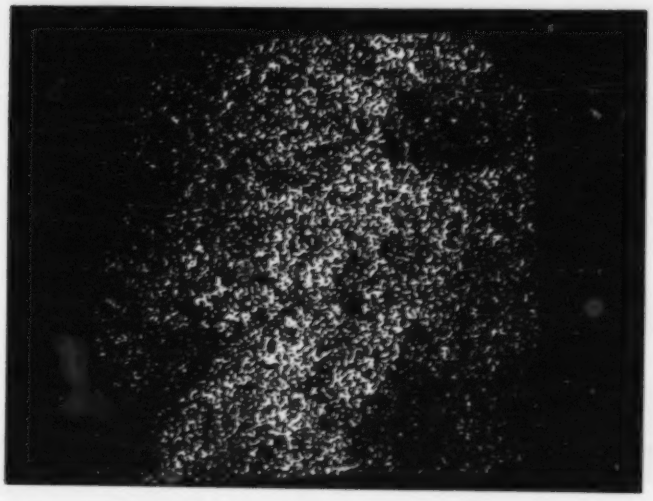
X400

Figure 14: Zr-3.0%Cu-4.5%Mo (Melt KU).
Arc-melted.
Electron-probe X-ray-scan photograph.
White areas: molybdenum-rich.



X400

Figure 15: Zr-3.0%Cu-4.5%Mo (Melt KU).
Arc-melted.
Electron-probe X-ray-scan photograph.
White areas: copper-rich.



X400

Figure 16: Zr-3.0%Cu-4.5%Mo (Melt KU).
Arc-melted.
Electron-probe X-ray-scan photograph.
White areas: zirconium-rich.

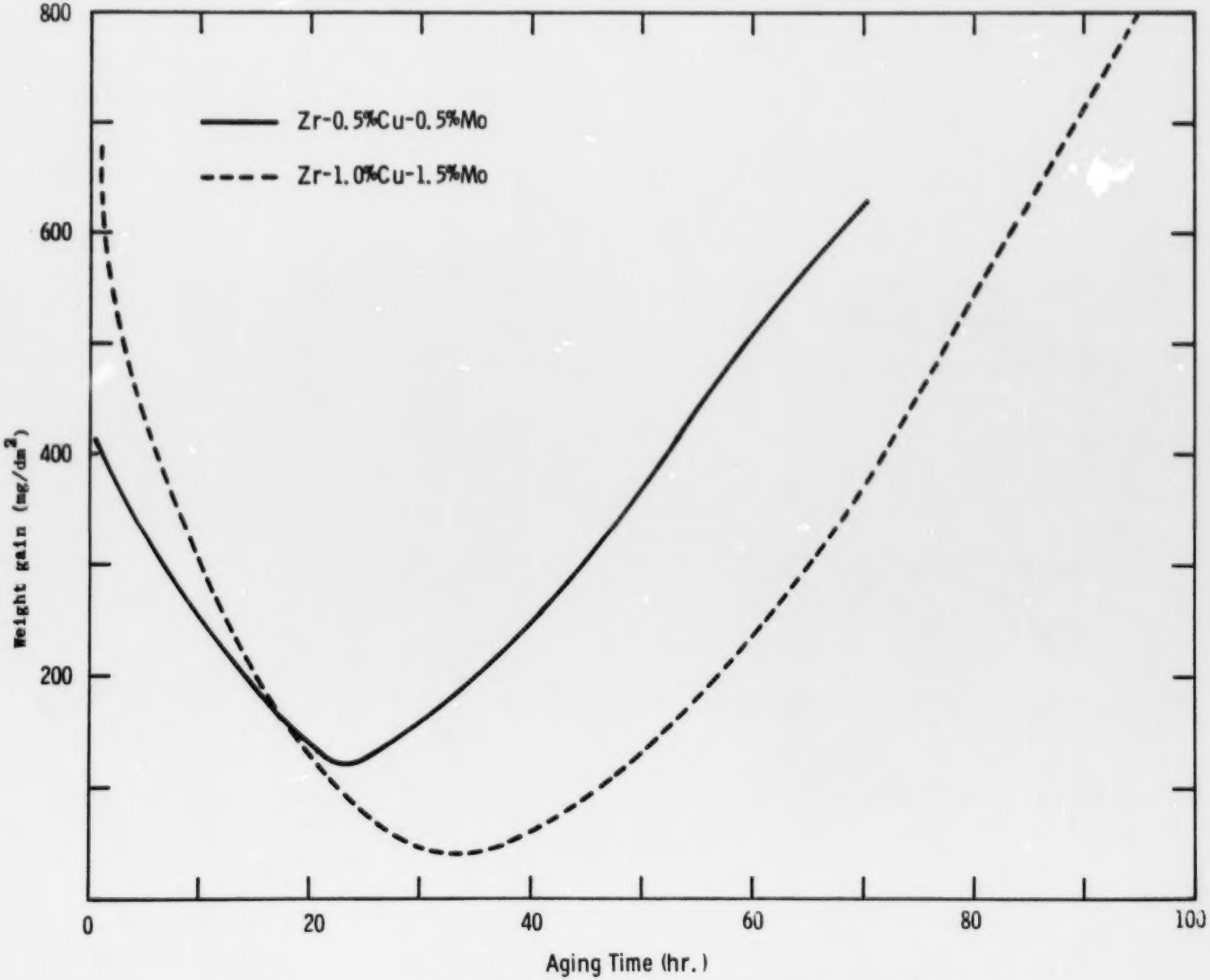
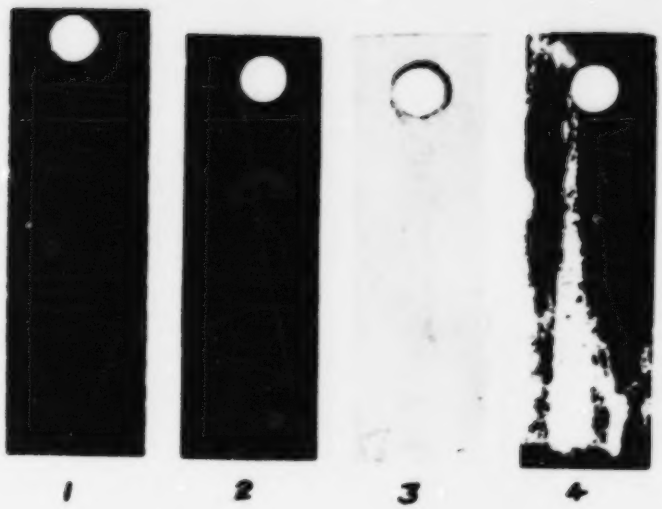
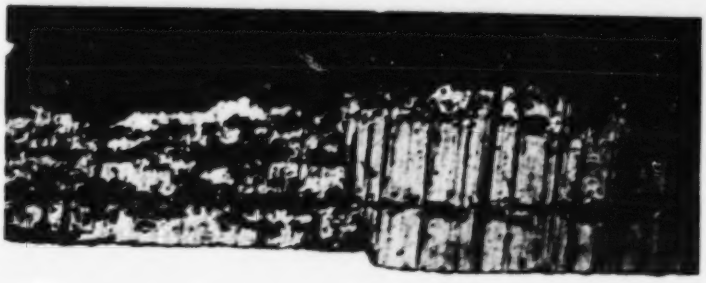


Fig. 17: Zr-Cu-Mo alloys, corrosion-tested at 400°C (750°F) and 1500 psi. ight gain versus aging time at 500°C (930°F).



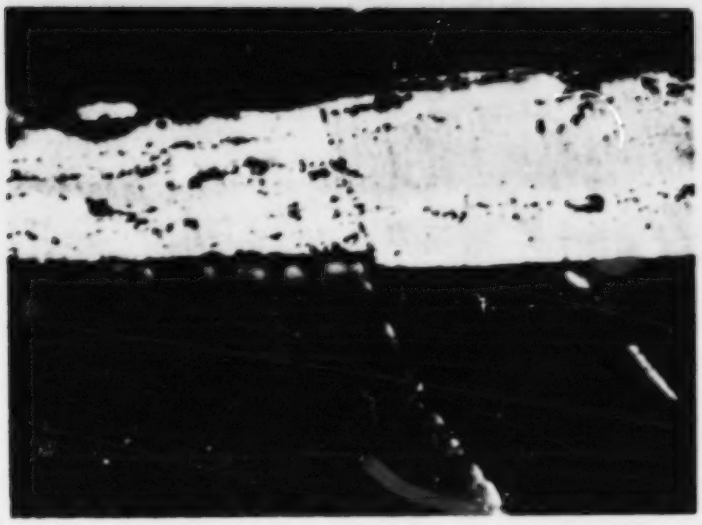
X2.5

Figure 18: Zr-1.0%Cu-1.5%Mo.
Quenched from 1000°C (1830°F), aged 500°C (930°F) for 0 hr (No. 1), 4 hr (No. 2), 100 hr (No. 3) and 48 hr (No. 4); corrosion-tested at 400°C (750°F) and 1500 psi for 400 hr.



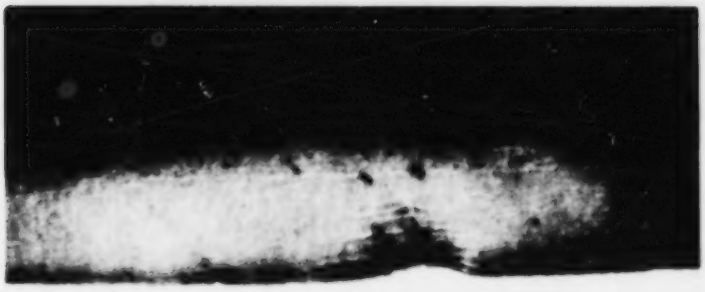
X500

Figure 19: Zr-1.0%Cu-1.5%Mo.
Quenched from 1000°C (1830°F); corrosion-tested for 400 hr at 400°C (750°F) and 1500 psi.
Cross section, as polished.



X500

Figure 20: Zr-1.0%Cu-1.5%Mo.
Quenched from 1000°C (1830°F);
corrosion-tested for 400 hr at 400°C (750°F)
and 1500 psi.
Cross section, mottled film.
Anodized, polarized light.

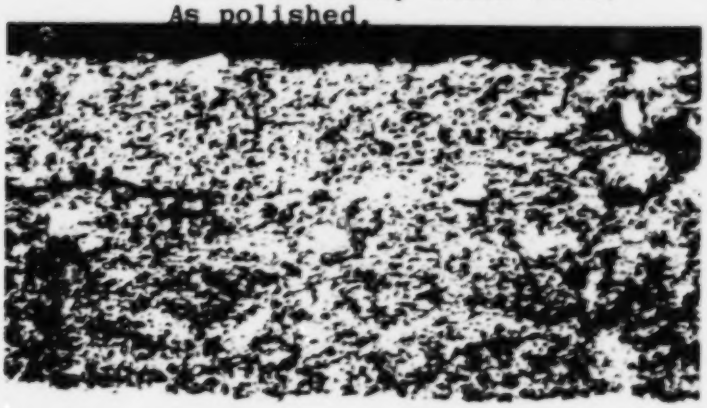


X500

Figure 21: Zr-1.0%Cu-1.5%Mo.
Quenched from 1000°C (1830°F),
aged at 500°C (930°F) for 4 hr;
corrosion-tested for 400 hr at 400°C (750°F)
and 1500 psi.
Cross section, black film.
As polished.

X500

Figure 22: Zr-1.0%Cu-1.5%Mo.
Quenched from 1000°C (1830°F),
aged at 500°C (930°F) for 48 hr;
corrosion-tested for 400 hr at 400°C (750°F)
and 1500 psi.
Cross section, black film.
As polished.



X500

Figure 23: Zr-1.0%Cu-1.5%Mo.
Quenched from 1000°C (1830°F),
aged at 500°C (930°F) for 100 hr;
corrosion-tested for 400 hr at 400°C (750°F)
and 1500 psi.
Cross section, white film.
As polished.

X10,000

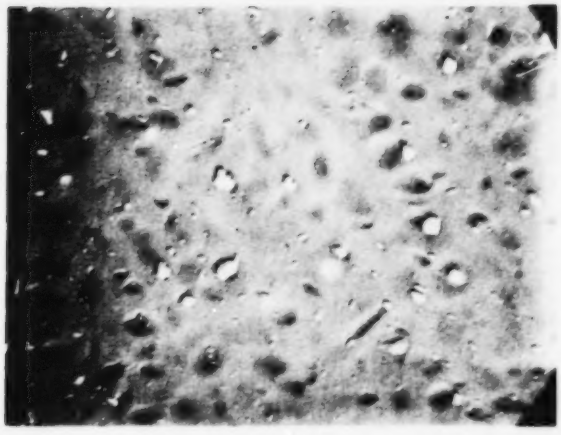
Figure 24: Zr-0.5%Cu-0.5%Mo.
Quenched from 1000°C (1830°F).
As polished.

X10,000

Figure 25: Zr-0.5%Cu-0.5%Mo.
Quenched from 1000°C (1830°F),
aged 500°C 8 hr.
As polished.

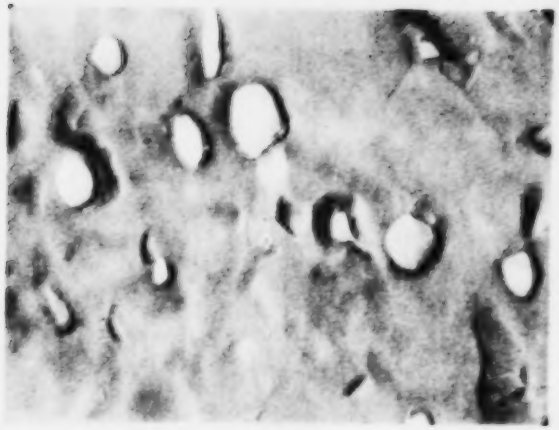
X10,000

Figure 26: Zr-0.5%Cu-0.5%Mo.
Quenched from 1000°C (1830°F),
aged at 500°C 24 hr.
As polished.



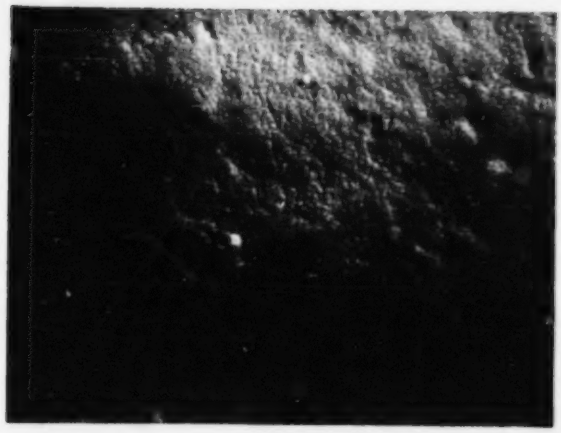
X10,000

Figure 27: Zr-0.5%Cu-0.5%Mo.
Quenched from 1000°C (1830°F),
aged at 500°C 100 hr.
As polished.



X10,000

Figure 28: Zr-0.5%Cu-0.5%Mo.
Annealed 700°C (1290°F) 1 hr.
As polished.



X10,000

Figure 29: Zr-0.5%Cu-0.5%Mo.
Quenched 1000°C (1830°F);
corrosion-tested 24 hr.

X10,000

Figure 30: Zr-0.5%Cu-0.5%Mo.
Quenched from 1000°C (1830°F),
aged at 500°C for 24 hr;
corrosion-tested 24 hr.

X10,000

Figure 31: Zr-0.5%Cu-0.5%Mo.
Quenched from 1000°C,
aged at 500°C (930°F) for 100 hr;
corrosion-tested 24 hr.

X10,000

Figure 32: Zr-0.5%Cu-0.5%Mo.
Annealed 700°C (1290°F) 1 hr;
corrosion-tested 24 hr.

- - - - - - - -

HMS:CFD:(PES)GT